

July 2005

Sampling for Volatiles in Louisiana Soils & Solids -Frequently Asked Questions
(FAQ)

This is a list of answers to frequently asked questions concerning sampling for volatiles in Louisiana soils and solid materials. If it does not address your question, or if you have additional comments, please feel free to e-mail or call the following personnel:

For field collection issues, contact Keith Horn, Keith.Horn@la.gov, or Heather Biletnikoff, Heather.Biletnikoff@la.gov, at 225/219-3236.

For sample analysis issues, contact Leonard Killmer, Leonard.Killmer@la.gov, or Elaine Sorbet, Elaine.Sorbet@la.gov, at 225/219-9800.

This FAQ list is divided into two sections; questions regarding EPA Method 5035, and questions dealing with EPA Method 5035 equivalent collection procedures for non-EPA methods.

EPA Method 5035

1. Q). Does EPA SW-846 Method 5035 apply to TCLP or SPLP analysis?

A). No.

2. Q). How can unconsolidated soils that will not form a cohesive plug be sampled?

A). These materials may be collected via a 5035 preserved vial method. They can be introduced into the vial using a laboratory scoopula or spatula -trying to minimally disturb the matrix of the sample. Alternately, these materials can be collected via the En Core[™] Sampler. The manufacturer gives the following instructions to sample sand, “Pull the plunger back to form an o-ring seal on the back end of the body and scoop or push sand into the sampler. When the cap is attached, the sand will be kept in a headspace-free state.” These procedures could be used to sample other unconsolidated materials. If using the En Core[™] Sampler in this manner, care must be taken to ensure that there is zero-headspace in the sampler, and that the o-rings are clear of material that could prevent a proper seal.

For further information on the use of the En Core[™] Sampler, see <http://www.ennovativetech.com/encore/encorefaqs.htm> -holdtimes. If other sample collection equipment for the method is approved by the LDEQ, in accordance with the procedures specified in Question 18 below, the user should follow the manufacturer’s instructions regarding unconsolidated soils.

3. Q). Can the En Core[™] Sampler be used to collect sediment or other wet material samples?

A). Yes, under currently allowed storage conditions and extraction times (i.e. storage at 4°C, and extraction within 48 hours of collection).

En Novative Technologies (the En Core[™] Sampler's manufacturer) found that if the material contained over 30% moisture, and the sampler was frozen, the water in the sample would expand and cause the seal on the En Core[™] Sampler to be compromised. These experiments with freezing the En Core[™] Sampler were conducted to demonstrate that a longer sample holding time for the En Core[™] Sampler would be appropriate. However, to date, the EPA has not extended the holding time for the En Core[™] Sampler. Therefore, the LDEQ requires adherence to the 48-hour-limit. Given that freezing is currently not an issue, neither is the moisture content of the sample.

If other sample collection equipment for the method is approved by the LDEQ in accordance with the procedures in Question 18 below, the user should follow the manufacturer's instructions for collection of unconsolidated material.

4. Q). Do the requirements of RECAP Appendix B, B.2.5.2. *Soil Investigations*, apply to EPA Method 5035 sampling?

A). Yes. For volatiles, the En Core[™] Sampler or 5035 preserved vials serve as the "clean sample container appropriate for the method" referenced in Paragraph 5 of *Soil Investigations* on Page B-8 of the RECAP Regulation. Special care must be taken to ensure that the sample containers are filled "immediately" following the splitting of the core sample taken from each interval.

The requirements of RECAP Appendix B do not allow for storage of soils to be sampled while headspace screening is being conducted. Even if material to be sampled is kept chilled in bags or other containers, volatiles are off-gassing as they are in the headspace screening aliquot. It is the off-gassed volatiles that are measured by headspace screening analysis. To meet RECAP investigation requirements, continuous down-hole soil sampling is required. Subsequently, samples for laboratory analysis are selected based on the headspace screening analysis results. Although this procedure increases the number of sample containers that require disposal, it is necessary to obtain accurate data. An alternative to continuous sampling is to co-locate a boring and obtain samples from those intervals identified in the second boring by the headspace screening of the original boring. The co-located boring approach must be included in a LDEQ approved Site Investigation Work Plan because it deviates from the requirements of RECAP Appendix B.2.5.2. The co-located boring approach is not approved for UST Motor Fuels Trust Fund reimbursement.

5. Q). Will EPA Method 5035A, the draft revision of Method 5035 be incorporated into the Louisiana rule in the near future?

A). Currently, there is no schedule to incorporate this revision into Louisiana's rule since this method has not been finalized. Therefore, its use is not authorized at this time. Information from EPA indicates that this draft method may be finalized in the Fourth Edition of SW-846 in late 2005.

6. Q). Why are field weight checks of preserved vials prior to collecting samples necessary?

A). This is a quality control procedure to ensure that the appropriate amount of preservative is present in the vial. Loss of preservative prior to introduction of the sample can result in inaccurate data. Methanol may evaporate from the vial prior to sample introduction and the method relies on a calculated ratio of solid to preservative to arrive at an accurate determination of the volatile concentration.

7. Q). What weight checks are required and what is their purpose?

A). Generally, the vials with preservative are weighed at the lab prior to fieldwork to 0.01 gram. This is to ensure that the vial contains the correct amount of preservative. A second weight check is performed immediately prior to sampling to determine the amount of any preservative losses due to evaporation or leakage, and verify that any losses are not equal to or greater than 0.2 grams. A third weight check of vial with sample is performed in the field to ensure that the sample aliquot is between 4.5 to 5.5 grams. The final weight check is made at the lab to 0.01 gram and compared to the baseline weight established by the initial weight check. The final weight is then used to calculate the concentration of volatiles in the sample.

8. Q). Is the Lock N Load™ Syringe, manufactured by Environmental Sampling Supply (and other similar devices), equivalent to the En Core™ Sampler?

A). No. As per the manufacturer's instructions and Standard Operating Procedure, the Lock N Load™ Syringe is used to obtain the 5-gram aliquot to fill the preserved vial in the field. The syringe is only to be used for field preservation, as are the: Terracore™ Sampler and the EasyDraw Syringe™ & PowerStop Handle™ both manufactured by En Novative Technologies, the Associated Design and Manufacturing Purge-and-Trap Sampler, and cut-off syringes (the last two are listed in the method for use with preserved vials).

9. Q). Is the use of the En Core™ Sampler mandated by EPA Method 5035?

A). No. The following options do not involve the use of field preservatives: the En Core[™] Sampler, and any other sampling device that may be approved by LDEQ as described in Question 18. The other option is to use preserved vials. Any unpreserved samples must be extruded from the sampler into preserved vials at the lab, or analyzed within 48 hours of collection.

10. Q). What labs can be used to analyze samples collected under these methods?

A). Only labs accredited by the Louisiana Environmental Laboratory Accreditation Program (LELAP) for the specific analytical method can be used to produce data for submission to LDEQ. A list of accredited labs can be accessed at <http://www.deq.louisiana.gov/portal/Portals/0/laboratory/web%20list%2002-22-06.doc>. However, these labs must be contacted to verify current accreditation for the specific analytical method(s) to be employed. You could also contact LDEQ Lab Services for analytical questions (see page 1 for contact information). It is important to discuss quantitation limits with the laboratory prior to submitting samples.

11. Q). The DEQ Feb. 27, 2002 letter that addresses Method 5035 states that, “the exclusive use of Method 5035 shall not apply to sites granted NFA Status by DEQ prior to July 1, 2002...” Does this statement imply that the exclusive use of the method will apply to sites that have not been granted NFA Status? This would mean that VOC soils data generated in the early 1990’s at a site that is still being evaluated later than July 1, 2002, would be invalid, even though the data passed a DQR as per Functional Guidelines as per EPA guidance, at the time it was generated?

A). That statement means that for sites NFAed prior to July 1, 2002, any further evaluation (such as a Phase II Environmental Site Assessment) should use methods consistent with those used at the time of closure (NFA = No Further Action). As stated in the LDEQ February 27, 2002 letter, data generated from samples collected prior to July 1, 2002, will be accepted by LDEQ. Therefore, even for sites not granted NFA Status prior to July 1, 2002, data generated from samples collected prior to July 1, 2002, will be considered valid data.

12. Q). The SW-846 Method 5035 (Section 2.1) specifies that approximately 5 grams of the soil sample is weighed in the field prior to placing into a pre-weighed vial with septum-sealed screw-cap that already contains methanol or a stirring bar and sodium bisulfate preservative. Undoubtedly, it will be hard for a field tech to maintain a balance capable of 0.01-gram resolution in typical field conditions. Would it be allowed to place the soil sample in the pre-weighed vial and let the lab measure a final weight, the difference in weight attributed to the soil sample?

A). No. EPA’s clarification of the method (available at <http://clu-in.org/goto.cfm?link=%2Fproducts%2Fregs%2Fsw846mem%2Ehtm&id=75>) addresses some of these issues. EPA states that, “Sample vials are weighed in the field before use.” There is an allowable variance of up to 0.2 grams for balances used to perform weight checks of vials in the field. Therefore, a field balance capable of

only a 0.1-gram resolution in typical field conditions is required. This is also adequate to verify that 5 grams of solid material, plus or minus 10% (i.e., 4.5-5.5 grams) is introduced to the vial per the method. The weight checks are important to perform in the field because the method requires that a known amount of solid be introduced into a known amount of preservative. Our experience is that the methanol evaporates, even from vials that appear to be properly sealed. If this loss is sufficient, the analytical results will be compromised. Although operation of a balance in the field can be somewhat challenging, there are some ways of mitigating the inherent difficulties in this task. The balance can be set up in the back of a van or SUV to protect it from the wind. All weight checks for the day can be performed prior to sampling. In our experience, it is easiest to tare out the vial weight, and then begin introducing solid until 4.5-5.5 grams are reached. Then, the final weight check performed in the lab will indicate the final soil weight once the baseline weight is subtracted. However, if weight checks are not made in the field, methanol loss could compromise the result.

13. Q). The method (4.5.3) allows use of disposable plastic syringes with the tip cut off instead of the En Core[™] Sampler, which can be pushed into the solid for collection and then used to extrude the sample into the preserved vial by depressing the plunger. The higher cost of the En Core[™] Sampler and its relatively greater diameter make this alternative attractive whenever practical. When is this alternative technique allowable?

A). Cut off syringes or other similar devices cannot be substituted for the En Core[™] Sampler, or any other sampling device approved by LDEQ as described in Question 18, because they serve different functions. The sampler must choose between the use of such collection and transport devices or preserved vials. The method allows the use of plastic syringes (or other similar devices, such as the Terracore[™] Sampler) to fill preserved vials with the required 5 grams of solid. Conversely, when the En Core[™] Sampler, or any other sampling device approved by LDEQ as described in Question 18 are used, the sampling device itself serves both to capture the required amount of sample and as the transport container.

14. Q). An average soil sampling apparatus consists of split spoon or Shelby Tube samplers that are 2 ft. in length. Typical soils in Louisiana are heterogeneous with silt and clay lens predominant. A single plunge using the En Core[™] Sampler into a clayey lens in the 2 ft. core will probably result in a different concentration than would result from a plunge into a silt lens in the same core. Is it acceptable to make multiple plunges with the syringe along the length of the core to better represent the entire sample interval?

A). No. The sampling tool must be filled in one operation to minimize the introduction of oxygen. Knowledge of the site's characteristics should be considered when selecting exactly where in the 2 ft interval to plunge the sampling device. Soil characteristics, including the occurrence of different layers within the 2 ft. interval,

should be examined with respect to the mobility and availability of the constituent of concern. The sampler should carefully document important considerations in this selection process. If there is a lack of complete information, the sampler should take discrete grab samples of each distinct soil layer using the appropriate sampling device. Please note that each individual plunge must completely fill the sample device and be analyzed separately. Appendix B of the Risk Evaluation/Corrective Action Program (RECAP) provides procedures designed to ensure that the highest concentration portion of each boring interval is sampled.

15. Q). The Method ([Section] 1.5) states that volatile, water-soluble compounds can be included in this technique, but quantitation limits by GC or GC/MS are approximately ten times higher because of poor purging efficiency. Will this cause a problem meeting screening option levels for these constituents?

A). This is not anticipated to have a significant impact. The primary problem we have encountered in meeting screening option standards is the same as previous methods: matrix interference. This problem should be addressed in the Data Quality Objectives (DQOs) portion of a sampling plan.

16. Q). The Method ([Section] 2.3.2) states that samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585. Is this still in accordance with the February 27, 2002 memo?

A). This is the procedure specified by EPA Method 5035. Therefore, it is in accordance with the February 27, 2002 memo. If it becomes necessary to use Method 3585, it should be documented in the sampling report how it was determined that the oily material was not soluble.

17. Q). Does EPA Method 5035 apply to EPA Method 8015B when collecting samples to be analyzed for petroleum hydrocarbons?

A). Yes, for Gasoline Range Organics (TPH-GRO) only, as described in Section 1.2 of EPA Method 8015B and Section 1.6 of EPA Method 5035.

18. Q). What samplers does LDEQ consider as “equivalent” to the En Core™ Sampler?

A). Currently none. However, the LDEQ has established a procedure for sampler manufacturers to have their products evaluated by the LDEQ and possibly accepted for use in Louisiana. There are two methods for such evaluation:

- The first option is to present the results of a performance evaluation directly to the LDEQ field sampling contacts listed at the beginning of this FAQ List. The LDEQ Solid VOC Sampling Workgroup will evaluate the performance data, and if it is acceptable, the

approved device will be listed here.

- The second option is to present to the LDEQ field sampling contacts, the results of an EPA review of a performance evaluation of the sampling device. The LDEQ Solid VOC Sampling Workgroup will evaluate the review of the performance data for acceptability in Louisiana.

EPA Method 5035 equivalent collection procedures for non-EPA methods

Appendix D of the October 20, 2003, Louisiana Department of Environmental Quality (LDEQ) Risk Evaluation/Corrective Action Program (RECAP) Regulation, authorizes three non-EPA methods for the analysis of petroleum hydrocarbon mixtures and fractions. These are the Massachusetts Department of Environmental Protection's (MDEP) VPH/EPH (volatile petroleum hydrocarbons/extractable petroleum hydrocarbon) Method (http://www.state.ma.us/dep/bwsc/vph_eph.htm -methods), the Texas Commission on Environmental Quality (TCEQ) Method 1006 (<http://www.tnrcc.state.tx.us/permitting/remed/techsupp/method1006.pdf>), and TCEQ Method 1005 (http://www.tnrcc.state.tx.us/enforcement/csd/qa/1005_final.pdf). The following FAQ's apply to these three methods.

19. Q.) Where are instructions for collection of samples for MDEP VPH analysis?

A) Appendix 4 of the Method for the Determination of Volatile Petroleum Hydrocarbons contains information on collection of VPH aliquots. It can be found at: <http://www.mass.gov/dep/bwsc/files/data/vph0504.pdf>.

When implementing these collection procedures in Louisiana, the following must be adhered to:

- Option 1: In-Field Methanol Preservation Technique, Step 4-Comment: The use of a field balance is not optional in Louisiana. Therefore, the use of volumetric marks is not applicable. Field weights of solid aliquots should be accurately weighed to +/-10%. Laboratory prepared methanol vials must be weight checked within 24 hours prior to use and be +/-0.1 g of the laboratory weight.

20. Q.) Where are instructions for collection of samples for TCEQ Methods 1005 and 1006 analysis?

A.) TCEQ Method 1006 has collection information in Section 7.0 of the Method (available at: <http://www.tnrcc.state.tx.us/permitting/remed/techsupp/method1006.pdf>), which references collection information in Section 6.0 of TCEQ Method 1005 (as modified by bullet 2 on page three of the TCEQ Method 1005), (available at http://www.tnrcc.state.tx.us/enforcement/csd/qa/1005_final.pdf) which then references TCEQ Guidance on the Use of EPA Method SW-846 5035.

When implementing these collection procedures in Louisiana, the following must be adhered to:

- Bulk sampling for volatile analysis (C₆–C₁₂) is never allowed in Louisiana.
- The use of a field balance is required in Louisiana. Field weights of solid aliquots should be accurately weighed to +/-10%. Unused aliquots collected for TCEQ Methods 1005 & 1006 cannot be used for other volatile analyses such as BTEX via EPA SW-846 8260B or 8021B (as stated in the second bullet of section 6.1 of TCEQ Method 1005). In Louisiana, it is required that aliquots for other volatile analyses under these methods be collected in strict accordance with EPA Method 5035 procedures.

21. Q.) What are the holding times for volatile aliquots of samples for TCEQ Methods 1005 and 1006?

A.) The three TCEQ references given above provide conflicting information on this issue. Therefore, The LDEQ requires adherence to the TCEQ Guidance on the Use of EPA Method SW-846 5035, Section 7.0 Laboratory Operations. The holding time for samples with no chemical preservative is 48 hours at $4 \pm 2^{\circ}\text{C}$. The sample can then be frozen or preserved at the laboratory according to the specific guidance given in the respective method. The holding time for bulk samples given in Section 7.3.3 is not applicable in Louisiana, as bulk samples are not allowed for volatile analysis.